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The Role of Temperature on Carbon Monoxide Production in Compartment Fires

Daniel T. Gottuk, Richard J. Roby & Craig L. Beyler

Hughes Associates Inc., 3610 Commerce Drive, Suite 817, Baltimore, Maryland 21227, USA

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ABSTRACT

The objective of this study was to assess the effect of temperature on carbon monoxide production in compartment fires in order to resolve the difference between global equivalence ratio–yield correlations obtained in simplified upper layer environments and more realistic compartment fires. The chemical reactivity of upper layer gases was studied using a detailed chemical kinetics model. An analysis of the modeling and experimental data in the literature provided insights into the effect of temperature on carbon monoxide production.

The effect of changing temperature on compartment fire upper layer composition is twofold: (1) *the generation of species in the fire plume is changed*; *and* (2) *oxidation of post-flame gases in the layer is affected. Elevated compartment temperatures correlate with increased fire plume temperatures and more complete oxidation of the fuel to* CO_2 *and* H_2O *within the plume. The layer temperature dictates post-flame oxidation in the layer. For most situations, upper layer temperatures below* 800K *indicate chemically unreactive layers. As such, combustion within the fire plume dictates final* CO *production in the compartment. Reactions in the upper layer dictate final* CO *levels when upper layer temperatures are about* 900K *and higher.*

1 INTRODUCTION

Studies of simplified upper layer environments (i.e. hood experiments by Beyler,[1,2] Toner,[3] and Morehart[4]) have shown that major species production rates can be correlated with the equivalence ratio using what is known as the global equivalence ratio (GER) concept. The

global equivalence ratio, ϕ, is defined as the ratio of the fuel volatilization rate to the air entrainment rate into the plume, normalized by the stoichiometric fuel-to-air ratio (mass basis). Since there were significant differences between aspects of the hood experiments and actual compartment fires, a series of tests was performed to determine if the GER concept was valid for more realistic fire environments.[5,6]

A 2·2 m^3 test compartment was used to investigate the burning of four fuels (hexane, PMMA, spruce, and flexible polyurethane foam) in compartment fires. A detailed description of the apparatus and a discussion of the results has been presented elsewhere.[5,6] It was shown that empirical correlations between the upper layer yields of major species and the global equivalence ratio existed for these compartment fires. Figure 1 shows the CO yield plotted vs the global equivalence ratio for hexane burned in the compartment and in Beyler's hood experiments.[7] The results reveal that the production of CO is primarily dependent on the compartment flow dynamics (i.e. the equivalence ratio). As can be seen, the correlations developed in the compartment fires are qualitatively similar to those developed by Beyler for simplified upper layer environments; however, quantitative differences exist.

For the range of equivalence ratios from about 0·5 to 1·3, higher CO production was measured in the hood experiments than in the compartment. Consistent with the higher production of CO, the yield

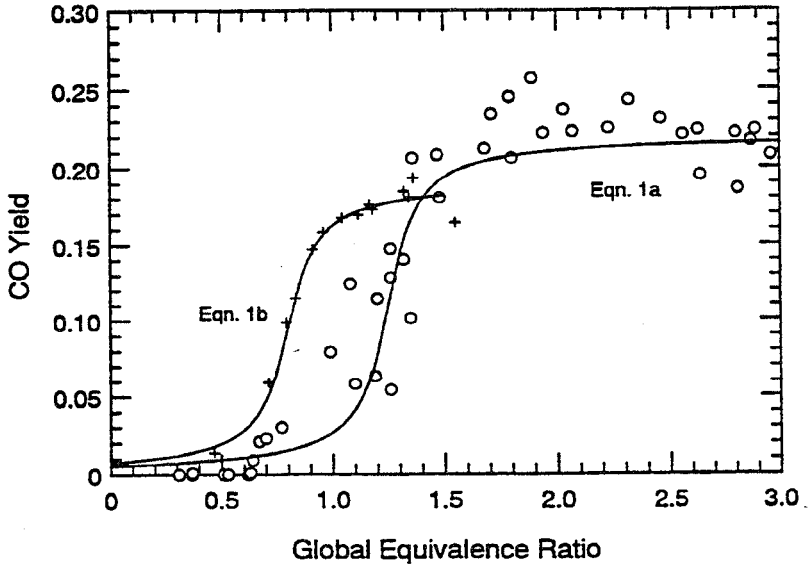

Fig. 1. GER CO yield correlations from Beyler's hood experiments (+) and from compartment fires (○) for hexane fires. Curve fits of the data are from equation 1 in Gottuk *et al.*[6]

of CO_2 is lower for the hood fires. For equivalence ratios above 1·3, the limited data suggest that compartment fire CO yields level out at a slightly higher value than do the hood yields.

The main difference in the fire environments between the two types of experiments was the upper layer temperature. For the region of discrepancy between equivalence ratios of 0·5 and 1·5, Beyler observed an average temperature of 556K compared with 970K observed for the compartment fires.[5,6]

The conversion of CO to CO_2 occurs via a reaction with an increasing temperature dependence for the range 500–2000K.[8] Therefore, as a result of the lower temperatures in the hood experiments, it is likely that chemical reactions were quenched in the post-flame (or upper layer) region. Since CO is the first product of hydrocarbon oxidation compared with CO_2,[8] quenching of the chemical reactions can lead to higher levels of CO at the expense of CO_2 production. The work of Tamanini illustrates this point.[9] Tamanini studied CO production within propane diffusion flames using an experimental apparatus which allowed the quenching of the fire plume at various heights. The results showed that low in the fire plume, CO production was at a maximum and, high in the flame, decreased to essentially zero as it oxidized to CO_2. This work suggests that a flame which is quenched higher up in the plume due to it being imersed into the upper layer of a compartment fire would produce higher levels of CO than a fire with little or no plume in the upper layer.

The primary goal of the study was to assess the effect of temperature on carbon monoxide production in compartment fires in order to resolve the difference in GER yield correlation results obtained from hood experiments and more realistic compartment fires. Towards this end, the first objective was to determine the reactivity of the upper layer gases in Beyler's experiments for a range of isothermal conditions characteristic of both the hood and compartment environments. It was hypothesized that, at temperatures characteristic of the compartment fire upper layers, the upper layer composition of Beyler's hood experiments would react and result in a composition similar to that in the compartment.

Due to the complex mixing processes and the significant temperature gradients in a compartment fire plume, current kinetic schemes are unable to model the complete behavior of the reacting flows and, therefore, are unable to predict final layer compositions. However, modeling of upper layer gas-phase chemistry is within the scope of current knowledge. Therefore, the study was conducted under the assumption that the generation of upper layer gases from a plume is

independent of upper layer properties and surrounding compartment effects, such as radiation. That is, at a given equivalence ratio, the plume generates the same products whether in the hood apparatus or in the compartment. The underlying assumption is that the upper layer and fire plume can be separated as two distinct control volumes. The validity of this assumption is discussed below.

2 PROCEDURE

Kee *et al.* at Sandia National Laboratories have developed a collection of computer codes and libraries known as CHEMKIN.[10] CHEMKIN provides the user with a framework to solve a set of differential equations describing gas-phase elementary reactions. The libraries perform various chemical and thermodynamic operations and provide thermodynamic data. The code, SENKIN,[11] which was modified to run on a VAX 11/780, was used to model the upper layer as a plug flow reactor. This code also performed sensitivity analysis to identify the key reactions for selected species. The user was required to formulate a kinetics model and driver code to run the SENKIN/CHEMKIN package.

Modeling of the upper layer was limited to either a perfectly stirred reactor (PSR) or a plug flow process. In short, the PSR is characterized by fast mixing and approaches the plug flow process (slow mixing) as the upper layer residence time approaches zero. A similar study performed by Pitts has shown no significant differences between results for upper layer compositions from the plug flow and PSR models.[12]

The kinetics model used was a subset of the Miller and Bowman mechanism,[13] primarily a C_1–C_2 hydrocarbon oxidation model. A listing of the mechanism used can be found in Gottuk.[5] The inclusion of a C_3–C_4 submechanism was of minor importance in modeling the oxidation of ethylene with a C_1–C_4 mechanism,[14] therefore, the use of a C_1–C_2 model was deemed sufficient. All initial hydrocarbons were represented as ethylene (C_2H_4), consistent with Beyler's measurements, which were used as initial inputs. Chakir *et al.*[15] showed that ethylene was the major constituent of unburned hydrocarbons for the oxidation of N-heptane for a range of equivalence ratios from 0·5 to 2·0 and temperatures from 900 to 1170K. It should also be noted that current knowledge limitations prevented the inclusion of soot formation and oxidation in the model.

The general procedure was to run a case corresponding to each of the 14 hexane tests performed by Beyler. Beyler's hexane-fueled upper

layer species measurements were used to define the initial mixture composition for the model. Only stable species (CO, CO_2, O_2, H_2O, H_2, C_2H_4, and N_2) were included. The inclusion of radicals in the initial composition was studied and proved to be of little significance as these species would equilibrate quickly compared with the stable species.

The use of Beyler's measurements provided a range of cases for ϕ from 0·47 to 1·55. Each case was run at the corresponding hood upper layer temperature and at a temperature representative of the compartment upper layer for fires with the same equivalence ratio. The model calculated species concentrations with respect to time for a period of 40 s, which was a typical residence time for the hood experiments. Residence times for the compartment fires studied were typically 10 s or less.

3 RESULTS

Figure 2 shows the measured and calculated CO concentrations at both the hood and compartment layer temperatures for hexane fires plotted vs the global equivalence ratio. The calculated concentrations are reported for a calculation time of 40 s. Figure 2 shows that the upper layer was unreactive at the hood temperatures as indicated by no

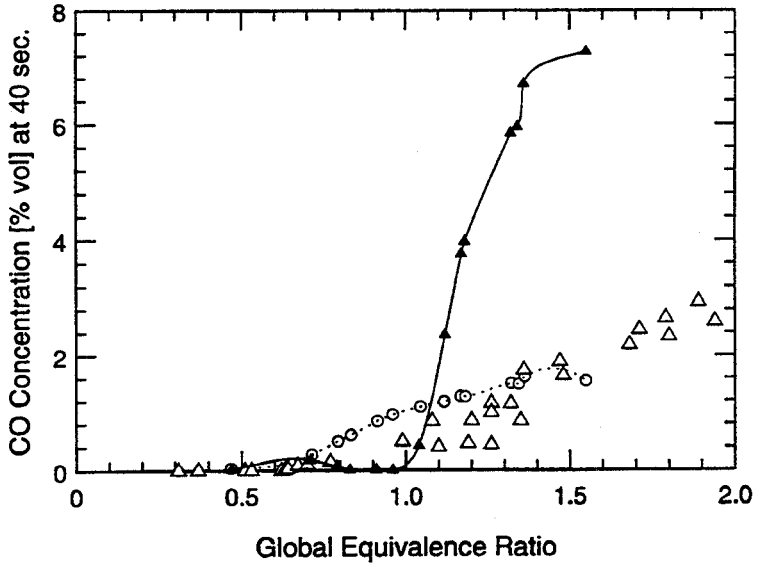

Fig. 2. Model-calculated CO concentrations vs global equivalence ratios for cases run at hood layer temperatures (dotted line) and cases run at compartment layer temperatures (solid line). The measured concentrations in Beyler's hexane hood experiments (○) also represent the initial values for the chemical kinetics model. (△) represents the measured concentrations in the hexane-fueled compartment fires.

change in the species concentrations from initial conditions (i.e. the dotted line and the O symbols). At the compartment temperatures, the composition is significantly changed. For overventilated fires ($\phi < 1$), CO is almost entirely oxidized, thus showing close agreement between the modeled results and the compartment fire measurements. Similar plots of modeled results for CO_2 and O_2 show corresponding increases in the CO_2 concentrations and decreases in the O_2 concentrations also consistent with the compartment fire measurements.[5]

The model results for underventilated ($\phi > 1$) conditions at elevated compartment fire temperatures (the solid line in Fig. 2) show a dramatic increase in the CO levels with increasing equivalence ratio. Oxygen concentrations are reduced to below 100 ppm. The CO_2 concentrations are relatively unchanged compared with the initial composition.[5] This indicates that the O_2 is utilized entirely for hydrocarbon oxidation and CO oxidation is essentially frozen.

Figure 3 shows the calculated major species concentrations plotted vs time for an overventilated case, $\phi = 0{\cdot}91$, at compartment fire temperatures. An equivalence ratio of 0·91 represents the region of ϕ about which the largest discrepancies occurred between the measured hood and compartment CO yields. The model predicts that the CO concentration initially rises as C_2H_4 is oxidized and the CO_2 remains fairly constant. When the C_2H_4 is consumed at about 4·5 s, CO begins to oxidize to CO_2 resulting in a net depletion of CO for times greater than 8 s.

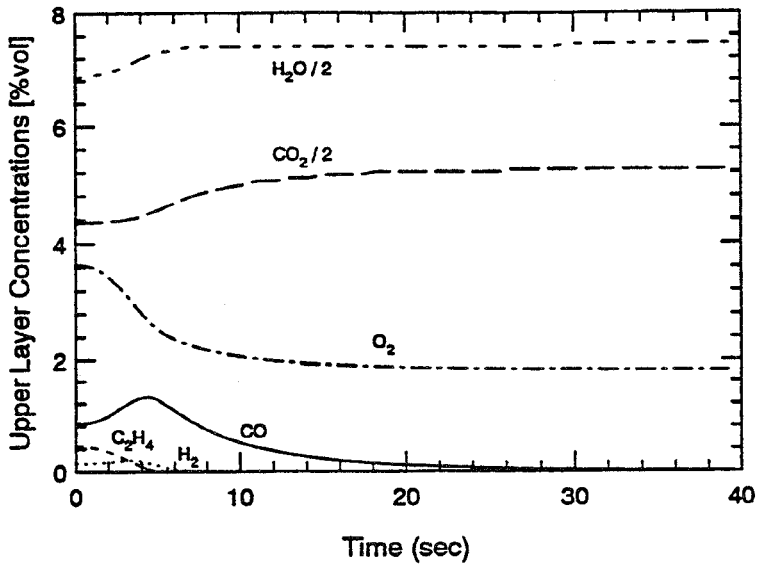

Fig. 3. Model-calculated major species concentrations vs time for $\phi = 0{\cdot}91$ and a temperature of 900K.

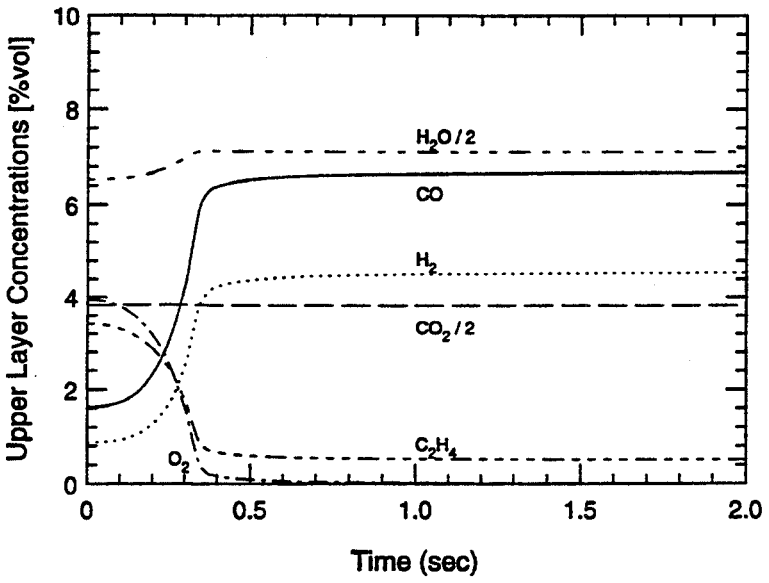

Fig. 4. Model-calculated major species concentrations vs time for $\phi = 1{\cdot}36$ and a temperature of 1000K.

Figure 4 shows the calculated major species concentrations plotted vs time for an underventilated case, $\phi = 1{\cdot}36$, at an upper layer temperature of 1000K. Again, at upper layer temperatures characteristic of compartment fires, the upper layer gases are quite reactive. The figure shows that for underventilated fires, the CO level rises quickly as C_2H_4 is oxidized. However, the oxygen is depleted before all the C_2H_4 is oxidized resulting in high CO concentrations and residual fuel. Carbon dioxide levels remain virtually unchanged.

The effect of temperature is presented in Fig. 5 which shows the CO concentration as a function of time and upper layer temperature for the case of $\phi = 0{\cdot}91$. As is clearly seen, the CO concentration in the upper layer is strongly dependent on both the temperature and the residence time. The initial rise in CO concentration is due to the oxidation of C_2H_4 as is shown in Fig. 3. The results show that a temperature between 800 and 850K is needed to promote the reactions governing hydrocarbon oxidation.

For underventilated conditions, CO increases with time and then plateaus. The time at which the CO concentration plateaus for the case of $\phi = 1{\cdot}36$ ranges from 36 to 0·8 s for temperatures of 850 and 1000K, respectively. These results demonstrate the strong temperature dependence of CO production. Carbon monoxide concentrations were not observed to increase significantly ($< 10\%$ change) at a gas residence time of 40 s for temperatures below 800K. Even at larger residence times, up to 300 s, the change in CO concentration was only 11% for

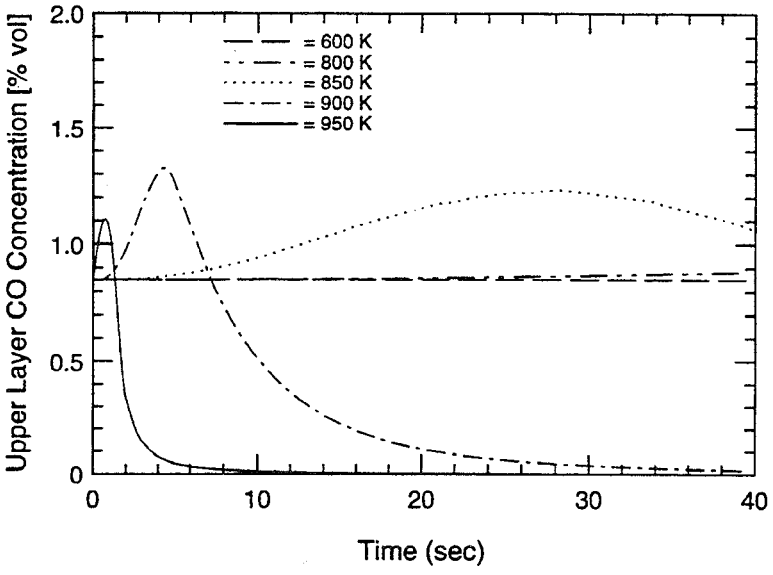

Fig. 5. Model-calculated CO concentration vs time at different isothermal conditions for $\phi = 0{\cdot}91$.

the case of $\phi = 1{\cdot}36$ at a temperature of 750K; at a temperature of 700K, there was only a 0·1% increase in CO.

The $\phi = 1{\cdot}36$ case at various isothermal conditions was used to judge whether an upper layer is unreactive. A layer was considered unreactive if a less than 1% increase in CO occurred. For this criterion, the upper layer of a compartment fire can be considered unreactive at a temperature of 800K or less for residence times less than 15 s, 750K for times less than 92 s, and 700K for times less than 760 s. Table 1 presents the time at which various percentage changes in CO occur in upper layer gases under different isothermal conditions.

TABLE 1

Time (s) at which Various Percentage Changes in CO Occur in Reacting Upper Layer Gases Under Different Isothermal Conditions. The Initial Gas Composition was for a Case of $\phi = 1{\cdot}36$ with a CO Concentration of 1·62vol%

Temperature (K)	*Percent change in* CO		
	1%	5%	10%
700	760	>1200	>1200
725	255	562	796
750	92	202	286
775	36	78	110
800	15	31	53

4 DISCUSSION

At temperatures characteristic of compartment fires, the model-predicted upper layer composition agrees extremely well with the compartment fire measurements for overventilated conditions. However, the model considerably overpredicts CO concentrations for underventilated fires. This can be seen in Fig. 2, which shows the comparison between model-calculated CO concentrations and the hexane compartment fire measurements.

For underventilated conditions, the model predicts CO concentrations up to four times higher than the concentrations measured in the compartment fires. Model-predicted CO_2 concentrations are as much as 26% lower than measured values, and the calculated O_2 concentrations of near zero are slightly lower than the compartment measurements of about 1%.

The modeling indicates that the oxidation of C_2H_4 is faster than CO oxidation. As can be seen in Fig. 3, significant CO oxidation does not occur until nearly all the available C_2H_4 is consumed. The CO concentration rises due to the initial hydrocarbon oxidation. Then, as the C_2H_4 concentration decreases, the remaining available O_2 is used for the conversion of CO to CO_2. Pitts,[12] in a similar study using Morehart's methane data, observed similar results. He states that the free radicals (H, OH, and HO_2) needed for CO and H_2 oxidation remain at low levels while significant amounts of unburned hydrocarbons are present, since they are considerably more reactive with hydrocarbons, such as ethylene. In the absence of hydrocarbons, the radical pool grows and CO is oxidized as in the overventilated cases.

According to the model, O_2 is depleted during hydrocarbon oxidation during underventilated conditions due to the high initial C_2H_4 levels. This results in high levels of CO and H_2 and remaining C_2H_4. There is negligible CO_2 production indicating that no CO oxidation occurs.

The results indicate, for $\phi < 1{\cdot}1$, that the elevated temperatures observed in the compartment fires ($T > 900$K) allow nearly complete oxidation of CO to CO_2 in the upper layer for overventilated and slightly underventilated conditions, while at the hood temperatures, the CO-to-CO_2 reaction is frozen resulting in elevated CO concentrations.

The discrepancy between the underventilated model results and experimental measurements of CO can be the result of two primary problems: (1) the gas-phase kinetics are incorrect; and (2) the modeling approach and assumptions are incorrect.

5 SUITABILITY OF CHEMICAL KINETICS

Studies of gas-phase kinetics modeling have shown good agreement with experimental results,[15–21] yet the kinetics of CO oxidation in the range of temperature from 800 to 1100K proves to be complex and still not fully understood.[12] Pitts investigated the use of three mechanisms on the formation of CO using Morehart's methane result ($\phi = 1{\cdot}76$) as initial conditions.[12] At a temperature of 1200K, CO concentrations agreed within 21%, however, at 900K, final CO concentrations varied up to about 65%. For both instances, the use of the methane oxidation mechanism of Dagaut *et al.* [18] produced the least CO. From the results and an analysis of the mechanisms, Pitts concluded that variations in CO concentration at temperatures of 900K are due primarily to differences in the rates of reactions involving HO_2, whereas for higher temperatures (i.e. 1200K), CO production is more sensitive to reactions involving H and OH.

The subset of the Miller and Bowman (MB) mechanism was also used to model the same case studied by Pitts above. At 1200K, the MB mechanism predicts similar CO concentrations as the mechanisms studied by Pitts. However, at 900K, the MB mechanism predicts a CO level approximately 70% higher than that using the methane oxidation mechanism of Dagaut *et al.*[18] This comparison suggests that the predicted CO concentrations using the Miller and Bowman mechanism may be as much as 70% high. However, this is not sufficient to account for the factor of 4 difference between experimental CO measurements and model-predicted values.

A sensitivity analysis was performed for the case of $\phi = 1{\cdot}36$ at a temperature of 1000K using the Miller and Bowman mechanism. Reflecting the fact that CO is an intermediate in the oxidation of hydrocarbons, the results indicate that both C_2H_4 and CO are most sensitive to the same 12 reactions. A listing of the key reactions for CO and C_2H_4 along with sensitivity coefficients can be found in Gottuk.[5]

At the completion of this study, the most current, applicable C_1–C_2 mechanism was that proposed by Dagaut *et al.* for ethane oxidation.[20] The top 12 key reactions for CO and C_2H_4 in the Miller and Bowman mechanism were updated with the rate data used in Dagaut's mechanism.

For the underventilated case of $\phi = 1{\cdot}36$, the updated Miller and Bowman mechanism resulted in a doubling of the time needed for reaction and a net decrease of 12% in CO formation. The decrease in the net CO production is due primarily to reduced C_2H_4 oxidation and not to CO oxidation. These results are consistent with those of Pitts

and further indicate that although the gas-phase kinetic mechanisms of CO oxidation continue to be refined, the associated uncertainty does not appear to be the cause of the large discrepancy between the predicted and experimental CO concentrations.

6 ANALYSIS OF THE MODELING APPROACH

Accepting the suitability of the kinetic mechanisms indicates that there is a problem with the assumptions of the modeling approach. Two assumptions that were necessary to perform the study are identified as possible sources of error. One is the assumption that the exclusion of soot formation in the model has no effect on CO formation. The second suspect assumption is that the generation of upper layer gases from a plume is independent of the upper layer properties and surrounding compartment effects, such as radiation. That is to say that at a given equivalence ratio, the plume generates the same products whether in the hood apparatus or in the compartment.

6.1 Exclusion of soot from the model

The formation of soot occurs primarily on the fuel side of a diffusion flame under conditions of low O_2 and high temperature gradients. Temperatures of 1300K and higher are needed to promote soot formation. The carbonaceous particles that are initially formed either oxidize in the flame or react further to form smoke. Since the modeled upper layer is not a flaming region and because of the existence of O_2 and the relatively low temperatures ($T < 1200$K), the formation of soot is unlikely. However, the interaction of existing soot in the initial composition with the gas-phase species is uncertain. Hydrocarbons are expected to be adsorbed by the soot particles, but due to the excess of hydrocarbons, it is doubtful that significant quantities would be consumed in this way to affect the net CO concentration. A second possibility is that soot may compete favorably for OH, thus decreasing gaseous hydrocarbon oxidation. However, unless soot oxidizes completely, net CO levels would not be expected to decrease. The effect of soot on the hydrocarbon and CO chemistry cannot be fully determined, so excluding soot chemistry from the modeling still remains as a possible source of error. However, it is unlikely that it accounts for the large overprediction of CO formation.

6.2 The fire plume as a source

The fire plume is a complex diffusion flame created from the buoyancy dominated flow of vaporizing fuel particles and the subsequent entrained air flow. Due to the variable local temperatures and species gradients, and turbulent mixing, the plume is difficult to characterize. However, study of the plume, in a global sense, provides useful insights into understanding the generation of upper layer species.

The results of Beyler's hood experiments suggest that the production of upper layer gases is independent of the structure and fluid dynamics of the flame. Beyler modified a 19 cm propane burner by including a 2·8 cm lip to enhance turbulence and the large-scale structure of the flame.[1] Compared with the no-lip burner, he reported that the flame was markedly changed and that air entrainment was increased by 30%. Yet, the upper layer species–equivalence ratio correlations were the same for both burners.

The insensitivity of species yields to the details of the flame structure is also suggested by the compartment fire hexane results shown in Fig. 1. The correlation includes data from fires utilizing various size burn pans and with a wide range of air entrainment rates, from 50 to 128 g/s. In several cases, nearly equal steady-state equivalence ratio fires were obtained with different sized pans and, consequently, quite varied burning rates and air entrainment rates (up to 50% different). Although the conditions varied significantly, the good correlation between yields and equivalence ratios suggests that the yields are not sensitive to the details of the flame structure.

However, data exist which indicate that the temperature of the plume has a significant effect on species production from the plume. It is reasonable to assume that the upper layer temperature difference between experiments is also reflective of a similar trend in the fire plume temperatures. An increase in the upper layer temperature can increase the fire plume temperature in two ways. For plumes that extend into the upper layer (as is true for all the hood experiments[1–4] and the compartment fires studied here), entrainment of hotter upper layer gases will result in increased plume temperatures. Secondly, an increase in the surrounding temperature reduces the radiant heat loss from the plume, thus resulting in a higher plume temperature.

Compared with the enclosed environment of the compartment fires, Beyler's hood setup resulted in fire plumes radiating to the relatively cold lab space below and entraining air which was not heated by a hot floor and lower walls. This, in addition to the fact that the upper layers in the hood experiments had lower temperatures, indicates that the

temperatures of the fire plumes in the hood experiments were lower than those in the compartment fires.

The effect of temperature on species generation in a fire plume can be found in the methane hood experiments of Morehart.[4,22] Morehart studied the effect of increasing temperature on layer composition by adding different levels of insulation to his hood. Except for the insulation, the test conditions (e.g. ϕ, equal to 1·45, and layer interface height) were held constant. The residence times of layer gases in the hood were calculated to be in the range 200–300 s. For the range of temperatures studied (500–675K), substantial increases in products of complete combustion and decreases in fuel and oxygen occurred with increasing layer temperature. The upper layer oxygen mass fraction was reduced by approximately 70% and the methane was reduced by 25%. Excluding one outlying data point, the CO concentrations increased by 25%. The temperatures of Morehart's upper layer were well below 700K. Therefore, based on the kinetics modeling of this study and that of Pitts,[12] these layers were unreactive at these low temperatures. It follows that the change in layer composition must have been due to changes in the plume chemistry. The more complete combustion can be attributed to an extension of the flammability limits (or reaction zone) in the plume due to the raising of the flame temperature.

The above discussion clearly demonstrates that changing the plume temperature substantially increases the consumption of O_2 and fuel and, primarily, increases the levels of products of complete combustion, with a small increase in CO. These conclusions are directly applicable to explaining the differences between the modeling results and the hexane compartment fire measurements. In order to correctly model the effect of temperature on layer reactivity, Beyler's layer composition should be modified to account for the temperature effect on plume generation of the initial layer gases. Based on this effect, the initial compositions used in the modeling would be expected to contain higher CO_2 and H_2O concentrations and lower O_2 and C_2H_4 concentrations due to more complete combustion in the plume. The net effect on the modeling results would be increased CO_2 levels and reduced CO levels from less incomplete hydrocarbon oxidation due to the lower availability of O_2 and C_2H_4 in the initial layer composition.

Direct modeling of the species in the plume is not feasible due to its complex nature. Nevertheless, the effects of modifying the initial composition to reflect more complete combustion in the fire plume can still be studied. For all the underventilated cases, the initial composition was modified by reacting all the C_2H_4 with O_2 to form CO_2 and H_2O. This was done under the criteria that the initial O_2 concentration was

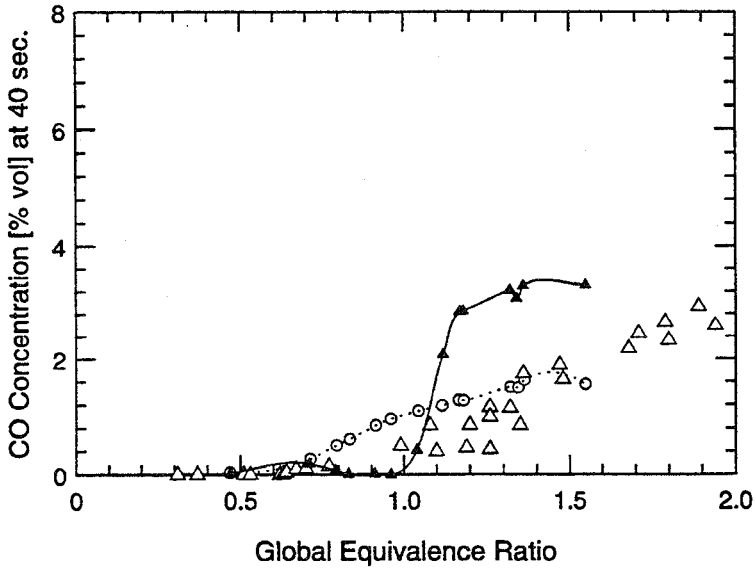

Fig. 6. Model-calculated CO concentrations vs global equivalence ratio for cases with initial compositions modified to reflect the effect of increased fire plume temperatures. The dotted line represents cases run at hood layer temperatures, and the solid line represents cases run at compartment layer temperatures. The measured concentrations in Beyler's hexane hood experiments (○) also represent the initial values for the chemical kinetics model. (△) represents the measured concentrations in the hexane-fueled compartment fires.

reduced to 1vol% for each case. This value is consistent with the typical level of O_2 measured in the underventilated compartment fires.

Figure 6 shows the CO results of the modeling using the modified initial composition compared with the compartment fire measurements. All cases were performed at the same temperatures (characteristic of compartment fires) as used in the initial study shown in Fig. 2. Overall, there is closer agreement between the model-calculated and measured CO concentrations. Consider the case of $\phi = 1{\cdot}36$ for example; the use of the modified initial composition resulted in a CO concentration of 3·2vol%, which is less than half that calculated for the original case. The modification resulted in the model-calculated CO concentration being a factor of two (instead of four) greater than the compartment fire measurements. These results indicate that excluding the effect of temperature on the plume chemistry is a primary reason for the discrepancy between model-calculated and experimental measurements of CO.

A comparison of the yield–equivalence ratio correlations for the four fuels burned in the compartment fires provides further evidence that CO production is dependent on temperature. The primary difference

between the correlations is that significant CO levels existed for overventilated spruce and polyurethane fires but not for the hexane or PMMA fires.[6] It should also be noted that the spruce and polyurethane CO yield data agree quite well as do the data for hexane and PMMA. In addition, the spruce and polyurethane CO yields agree well with those of various fuels burned in the hood experiments. Beyler's study of eight fuels (all with upper layer temperatures below 650K) shows that the production of CO in upper layer environments is basically independent of fuel type for overventilated and slightly underventilated fires.[1] Therefore, the difference between the compartment fire yield correlations is believed to be a result of the upper layer temperature effect.

For the region of interest between $\phi = 0{\cdot}6$ and $\phi = 1$, the spruce and polyurethane fires typically had average upper layer temperatures of 850K and lower, compared with temperatures of 920K and higher for hexane and PMMA fires.[5,6] These data are consistent with the chemical kinetics results that temperatures between 800 and 900K can be taken as the region in which CO oxidation to CO_2 is incomplete. The temperatures above 920K for PMMA and most hexane fires resulted in near complete CO oxidation as indicated by low yields compared with the high yields for wood and polyurethane.

7 CONCLUSION

This study has shown that the production of CO in compartment fires as correlated by the GER concept is also dependent on temperature. The effect of changing temperature on compartment fire upper layer composition is two-fold: (1) the generation of species in the fire plume is changed; and (2) the oxidation of post-flame gases in the layer is affected. Elevated compartment temperatures correlate with increased fire plume temperatures and more complete oxidation of the fuel to CO_2 and H_2O within the plume. The layer temperature dictates post-flame oxidation in the layer.

Upper layer temperatures below about 800K indicate fairly chemically unreactive layers. As such, combustion within the fire plume controls the final CO levels that would be measured in the upper layer. For underventilated conditions, CO concentrations will increase with increasing temperature.

Upper layer temperatures of about 900K and higher allow nearly complete oxidation of CO to CO_2 for overventilated and slightly underventilated conditions. Since the layer is chemically reactive at these temperatures, it dictates final CO production. For

underventilated fires, both chemical kinetics modeling and experimental results indicate that higher temperature environments will result in slightly higher CO yields due to increased hydrocarbon oxidation.

For underventilated conditions, two mechanisms affecting net CO formation compete (CO and hydrocarbon oxidation). Increasing the temperature above 900K depletes CO by accelerating the CO-to-CO_2 conversion. However, with increasing equivalence ratios, incomplete oxidation of unburned hydrocarbons increases the CO production. Since hydrocarbon oxidation is much faster than CO oxidation, net CO levels increase with equivalence ratio as unburned hydrocarbon concentrations increase.

The study was successful in resolving that the difference between the GER yield correlations obtained from simplified upper layer experiments and those obtained in more realistic compartment fires was a result of the stated fire plume and upper layer temperature effects. Therefore, it is concluded that the GER concept is valid; however, the effect of temperature must be considered. High CO concentrations can be created even for overventilated burning conditions if upper layer temperatures are below about 800K, which will result in freezing out the CO-to-CO_2 reaction.

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